

**Kinetics and Mechanism of Network Formation in a Sodalite-type Halozeotype**

S. J. Goettler (NCSU), J. Hanson (NSLS), and J. D. Martin (NCSU)

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**Introduction:** In order to gain control in the design of new materials, there is growing interest in understanding the mechanisms of solid state reactions. Specifically with respect to templated syntheses of open framework materials, the reactions are generally understood to consist of many components including: starting material dissolution, condensation and aggregation of  $\text{MX}_n$  tetrahedra, incorporation of templates, as well as nucleation and growth of the crystals. Recent *in situ* diffraction studies of the mechanism of the gel synthesis of zeolites clearly indicated that dissolution of the starting materials is frequently the rate-determining step of the reaction.<sup>1</sup> Our copper-zinc halide halozeotype materials (CZX-1 is isomorphous with sodalite), being synthesized from melt reactions,<sup>2</sup> or from the devitrification of their amorphous network,<sup>3</sup> provide a solventless system that allows us to bypass the rate-determining step of solvent dissolution and interrogate mechanistic contributions of network dimensionality, and framework nucleation and growth.

**Methods and Materials:** Samples of CZX-1,  $[\text{HN}(\text{CH}_3)_3][\text{CuZn}_5\text{Cl}_{12}]$ , were loaded into 0.7 mm fused silica capillaries, melted, and quenched into an ice bath to form a glass. Samples were heated to isotherms between 65 °C and 95 °C using a forced air heater, and time resolved diffraction data were collected using the MAR345. Diffractograms were obtained by full ring integration of the image plates. The fraction transformed was obtained as the average of the integrated area of six reflections, normalized to 100% for the complete reaction.

**Results:** An example of the TRXRD for the 75 °C isotherm demonstrating the crystalline growth from the amorphous sample is shown in Figure 1a below. The normalized data for four isotherms are given in Figure 1b. No crystallization reaction was observed for isotherms below 60 °C, the glass transition temperature for this material. When plotted as a function of reduced time ( $t/t_{0.5}$ ) these isotherms are superimposable indicative of an isokinetic process across this temperature range. These data are very well fit by an Avrami-Erofe'v nucleation and growth model, eq. 1, from which both the dimensionality of crystal growth and the rate constant can be extracted. These four isotherms indicate an average Avrami exponent  $n = 3.7$ . The temperature effect on the rate constant exhibits Arrhenius behavior (inset of Figure 1b) with an activation energy of 120 kcal/mol.

**Conclusions:** The Avrami exponent of 3.7 is indicative of a framework formation mechanism that proceeds with three-dimensional acceleratory growth, but that is also impacted by a slight deceleratory nucleation process. The three-dimensional framework growth is consistent with the cubic symmetry of the sodalite lattice that is formed. The nucleation process is likely impacted by a charge ordering of the templates.

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**References:**

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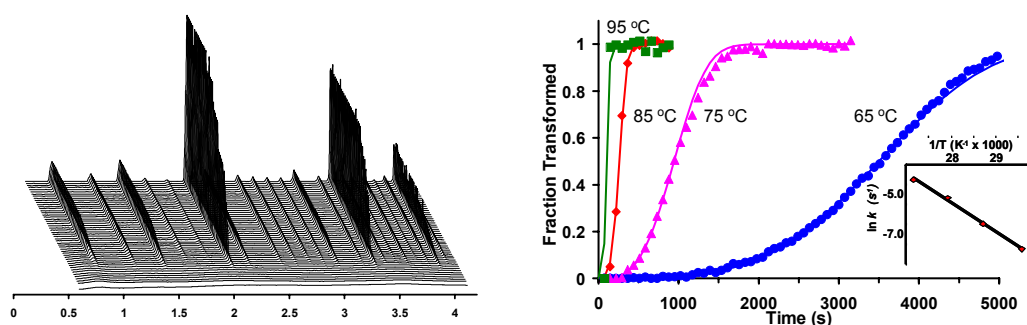


Figure 1. a) Time resolved powder diffraction data from the 75 °C isotherm. b) Plot of the fraction transformed as a function of time for 65 °C, 75 °C, 85 °C and 95 °C isotherms (symbols are experimental points and the solid line is the fit to the Avrami-Erofe'v model. An Arrhenius plot is an inset in the lower right.